Electronic supplementary Information:

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Role of halogen···halogen interaction in the 2D crystallization of n-semiconductors at the liquid-solid interface

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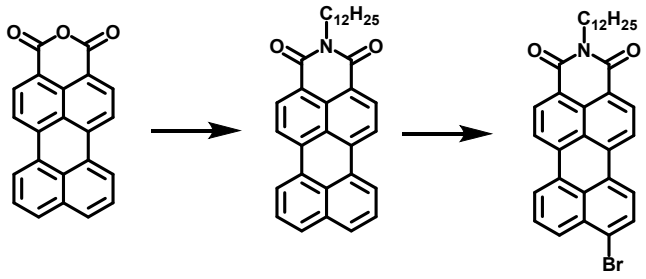
Experimental section

Synthesis of n-semiconductors

PMI and Br-PMI were synthesized according to the reported methods developed by prof. Klaus Müllen.[1]



PMI **Br-PMI**

PMI ^{1}HNMR ($CDCl_3$, 400 MHz, 298 K): δ= 8.25 (d, 2H), 8.09 (d, 2H), 7.99 (d, 2H), 7.74 (d, 2H), 7.45 (d, 2H), 4.12 (t, 2H), 1.80-1.70 (m, 2H), 1.47-1.23 (m, 18H), 0.88 (t, 3H). ^{13}CNMR ($CDCl_3$, 100 MHz, 298 K): δ = 163.8, 136.7, 134.2, 131.1, 130.8, 129.4, 128.9, 127.6, 126.9, 126.4, 123.4, 120.8, 119.9, 40.6, 32.1, 29.8, 29.8, 29.8, 29.6, 29.5, 28.3, 27.4, 22.8, 14.3. MS (EI): m/z (M^+) = 489 (calcd for $C_{34}H_{35}NO_2$: 489).

Br-PMI ^{1}HNMR ($CDCl_3$, 400 MHz, 298 K): δ= 8.11 (d, 1H), 8.06 (d, 1H), 7.91 (d, 1H), 7.82 (d, 1H), 7.72 (d, 1H), 7.62 (d, 1H), 7.51 (d, 1H), 7.47 (d, 1H), 7.34 (t, 1H), 4.09 (t, 2H), 1.78-1.68 (m, 2H), 1.50-1.22 (m, 18H), 0.88 (t, 3H). ^{13}CNMR ($CDCl_3$, 100 MHz, 298 K): δ = 163.4, 135.5, 135.4, 132.4, 130.8, 130.8, 129.6, 128.9, 128.9, 128.3, 128.3,

127.7, 125.9, 125.5, 123.7, 123.0, 121.0, 120.1, 119.8, 40.7, 32.1, 29.8, 29.8, 29.6, 29.5, 28.3, 27.4, 22.9, 14.3. MS (EI): m/z (M^+) = 567 (calcd for $C_{34}H_{34}BrNO_2$: 567).

General process for STM experiments

All STM experiments were performed at room temperature (20-25℃) using the MultiMode 8 system with the NanoScope V controller (Bruker). The STM images were obtained in the constant current mode. The STM tips used in this research were mechanically cut from a Pt/Ir wire (80/20, diameter 0.25 mm). Three kinds of molecules, PMI, Br-PMI and TBB (98%, Tokyo Chemical Industry) were dissolved in 1-octanoic acid (98%, Tokyo Chemical Industry) and 1-phenyloctane (98%, Tokyo Chemical Industry), respectively. After heating and dissolving, take a drop of them onto a freshly cleaved surface of Highly-Oriented Pyrolytic Graphite (HOPG, grade ZYB, Advanced Ceramics Inc, Cleveland, OH). Detailed imaging conditions are given in the corresponding figure captions. The underneath graphite lattice was obtained by lowering the sample bias immediately after recording the monolayer images.

Computational simulation

The molecular geometries of PMI and Br-PMI were fully optimized by density functional theory (DFT) at the B3LYP/6-31G(d) level, as implemented in Gaussian 09 software package. The molecular electrostatic potentials and HOMO and LUMO were then obtained using GaussView 5.0.

The model molecular assembled structures were optimized using the Forcite module of Materials Studio 7.0. The DREIDING force field was implemented for the geometry optimizations. The initial supramolecular structures were inspired from the high-resolution STM images observed experimentally.

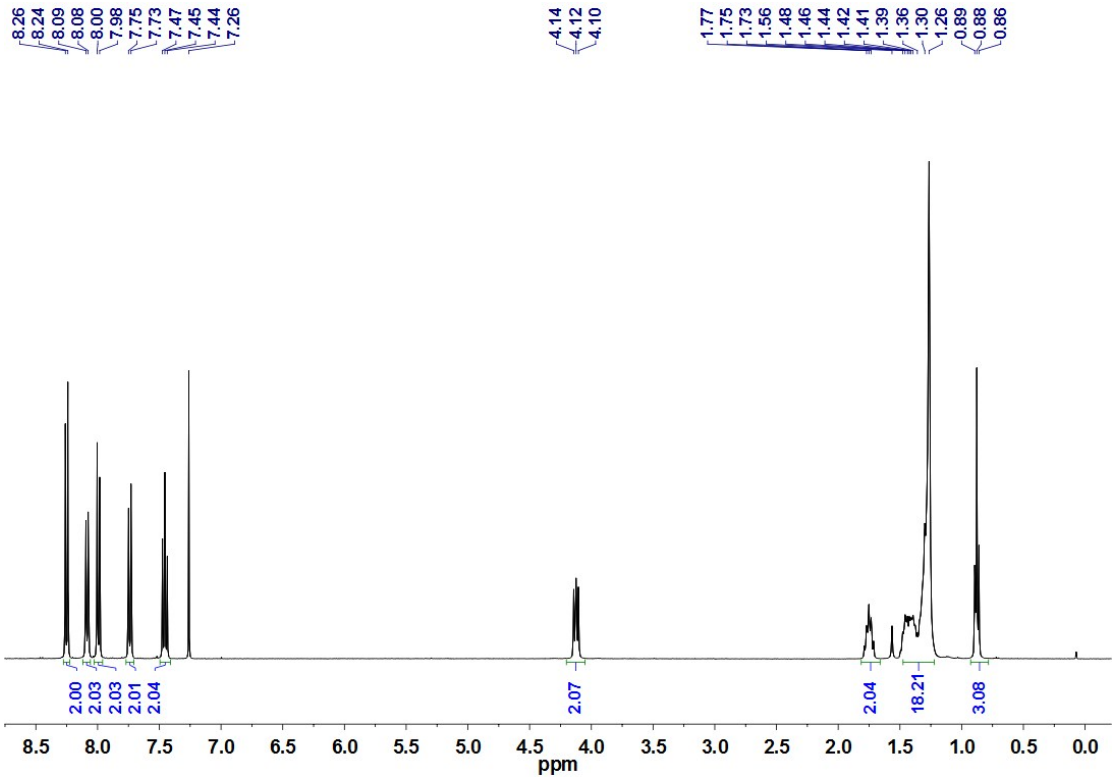


Fig. S1 ^{1}HNMR spectrum of PMI.

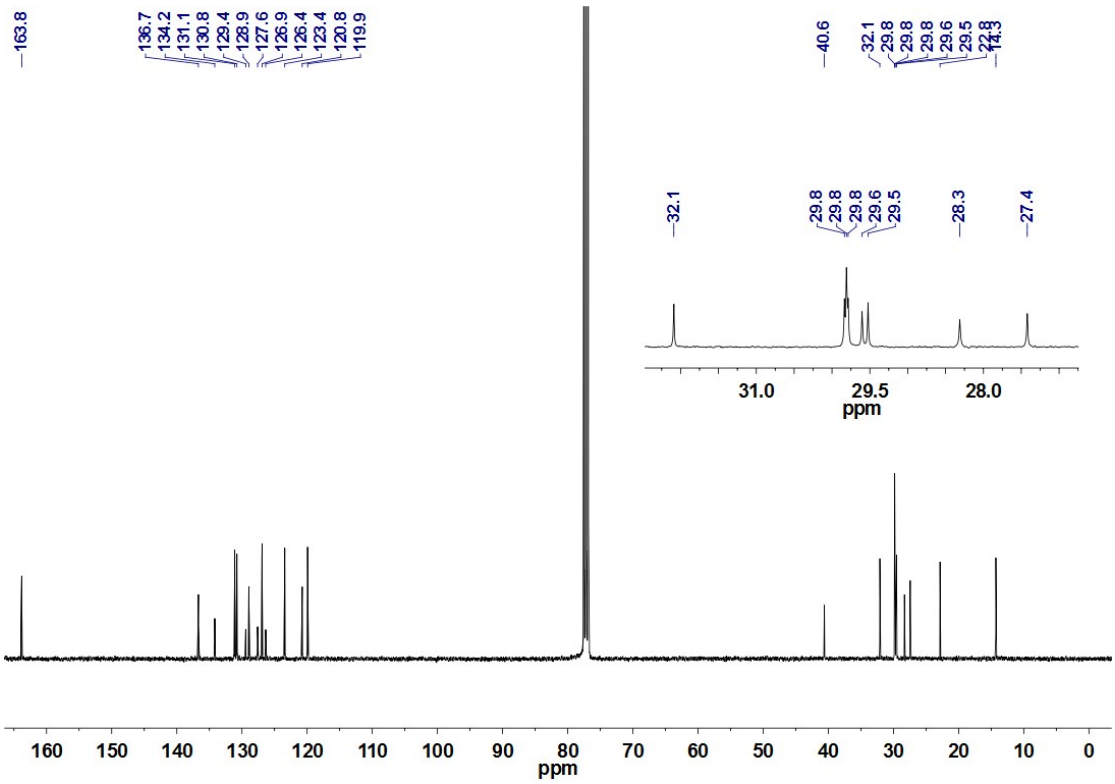


Fig. S2 ^{13}CNMR spectrum of PMI.

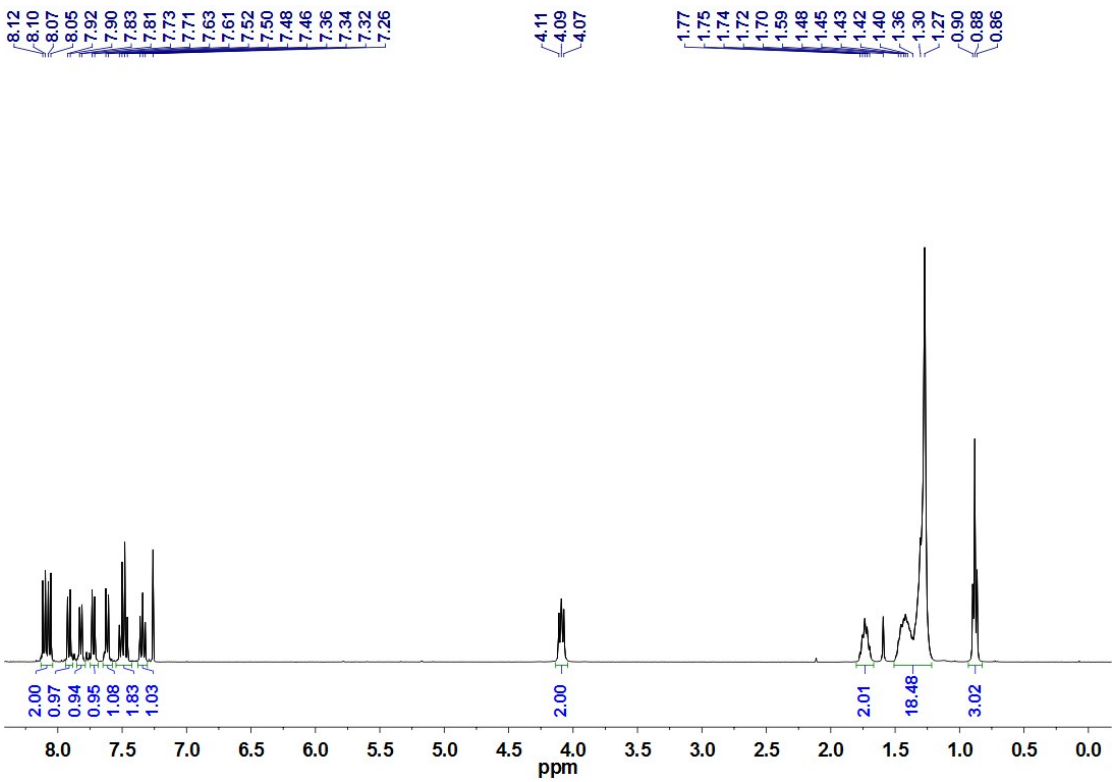


Fig. S3 ^{1}HNMR spectrum of Br-PMI.

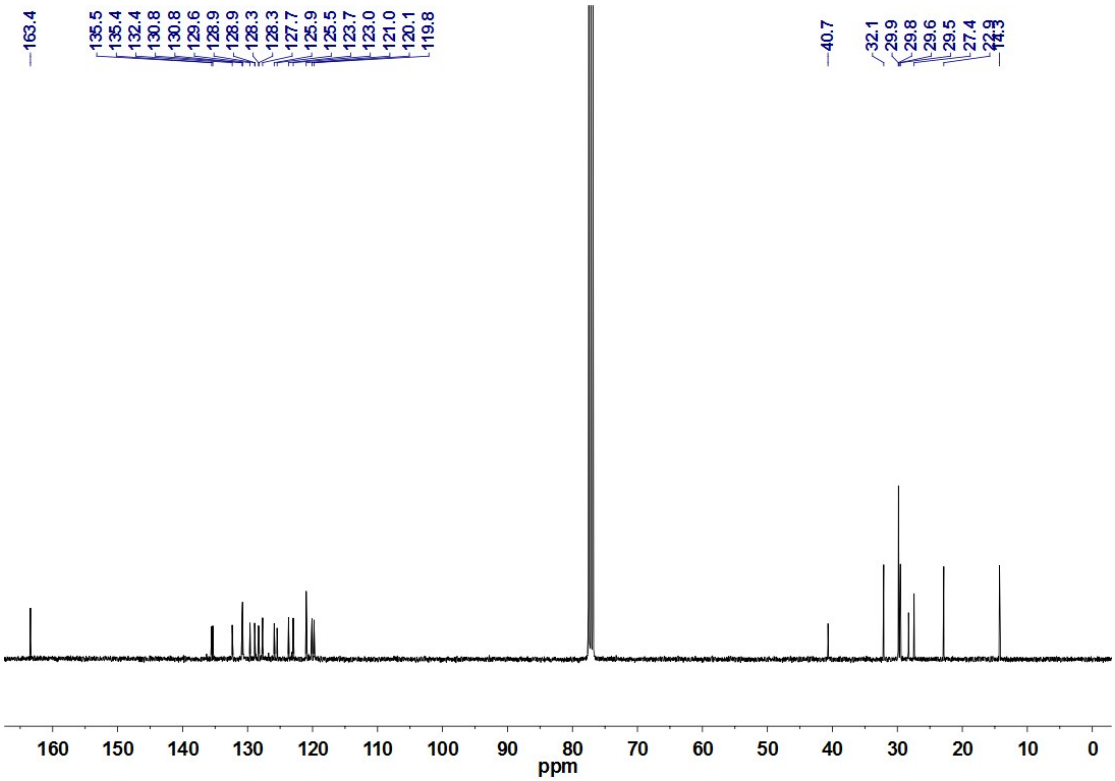


Fig. S4 ^{13}CNMR spectrum of Br-PMI.

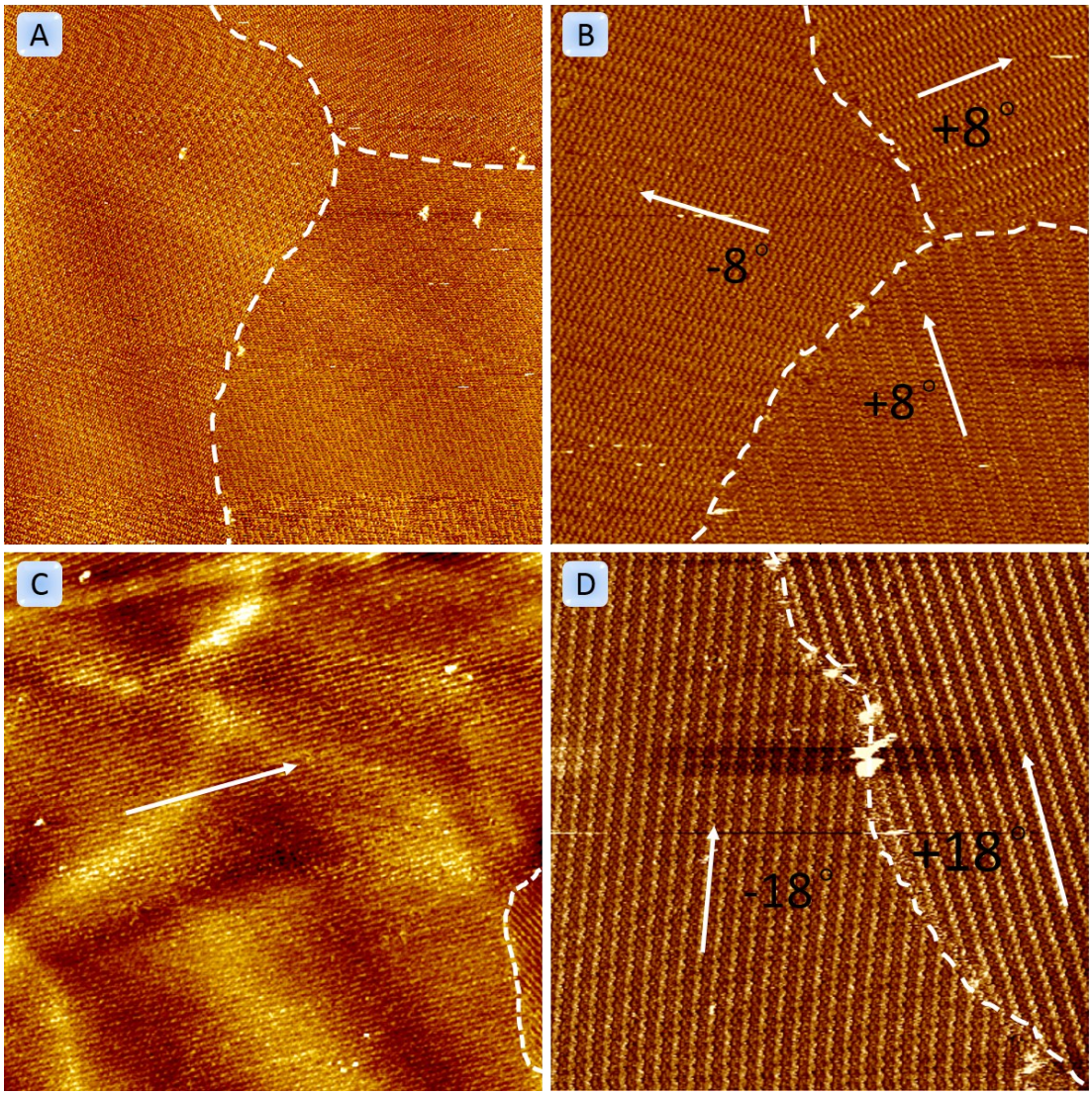


Fig. S5 Large scale STM images of A, B) PMI and C, D) Br-PMI at the 1-octanoic acid-HOPG interface. A, C) (300 × 300 nm^2); B, D) (100 × 100 nm^2). Imaging conditions: A, B) I_{set} = 60 pA , V_{bias} = – 800 mV; C) I_{set} = 115 pA, V_{bias} = – 650 mV; D) I_{set} = 90 pA, V_{bias} = – 700 mV. In image B and D, domains with opposite chirality with respect to the HOPG substrate were indicated.

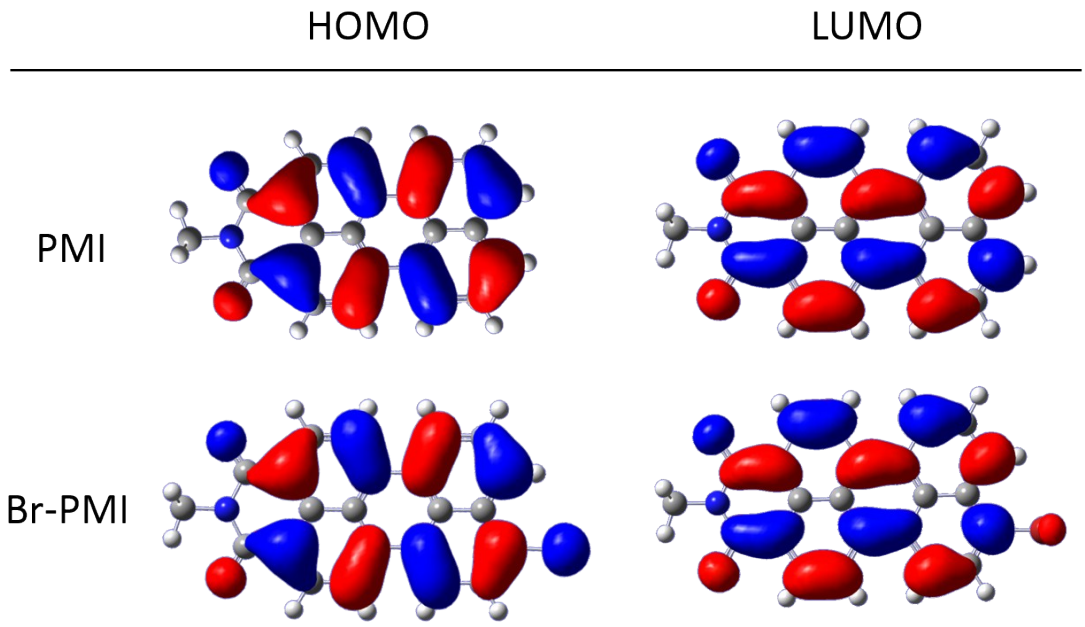


Fig. S6 Pictorial representations of HOMOs and LUMOs for Br-PMI and PMI.

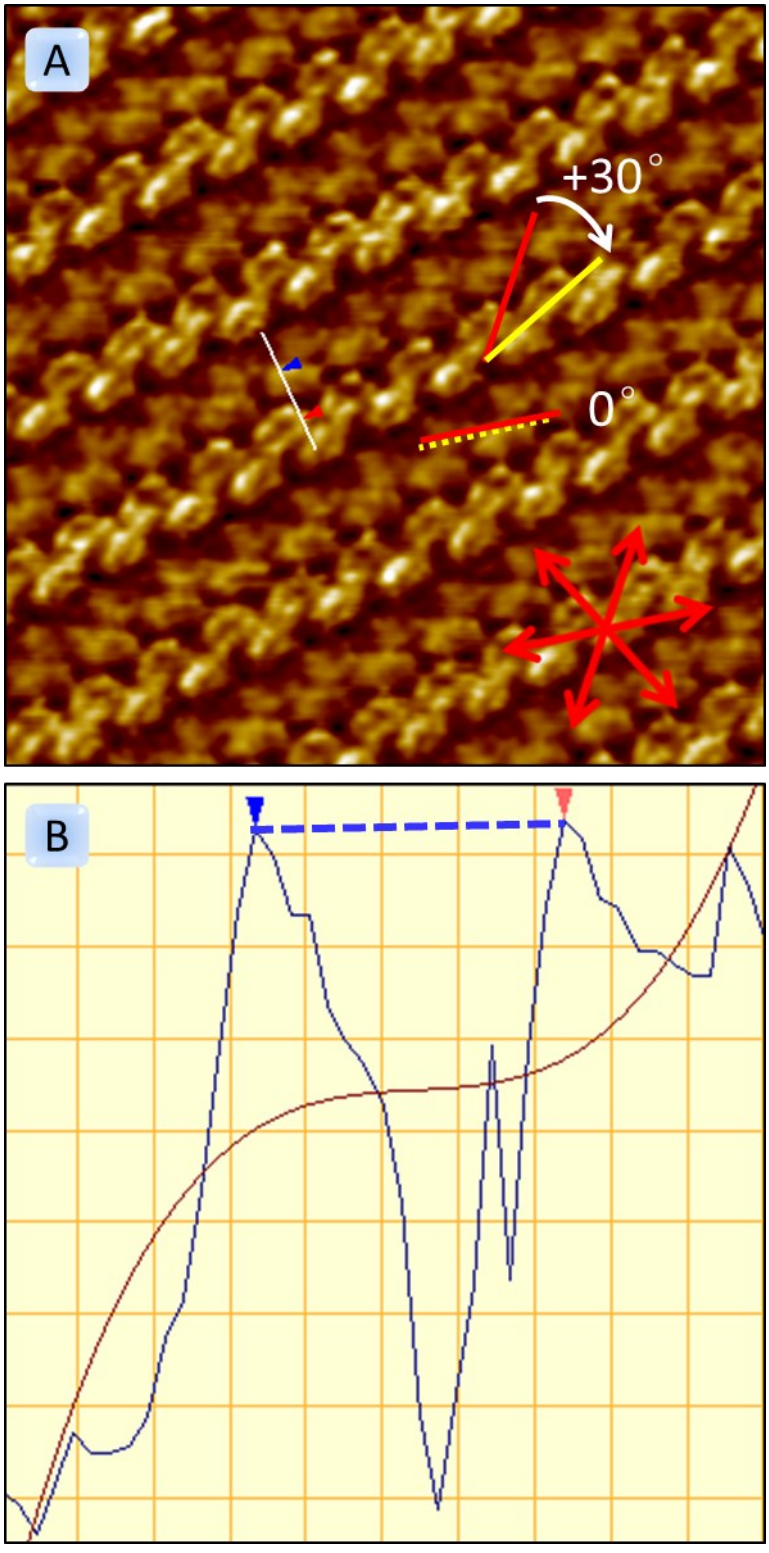


Fig. S7 A) STM image of Br-PMI. B) Section profile across the Br-PMI in bright and dark rows.

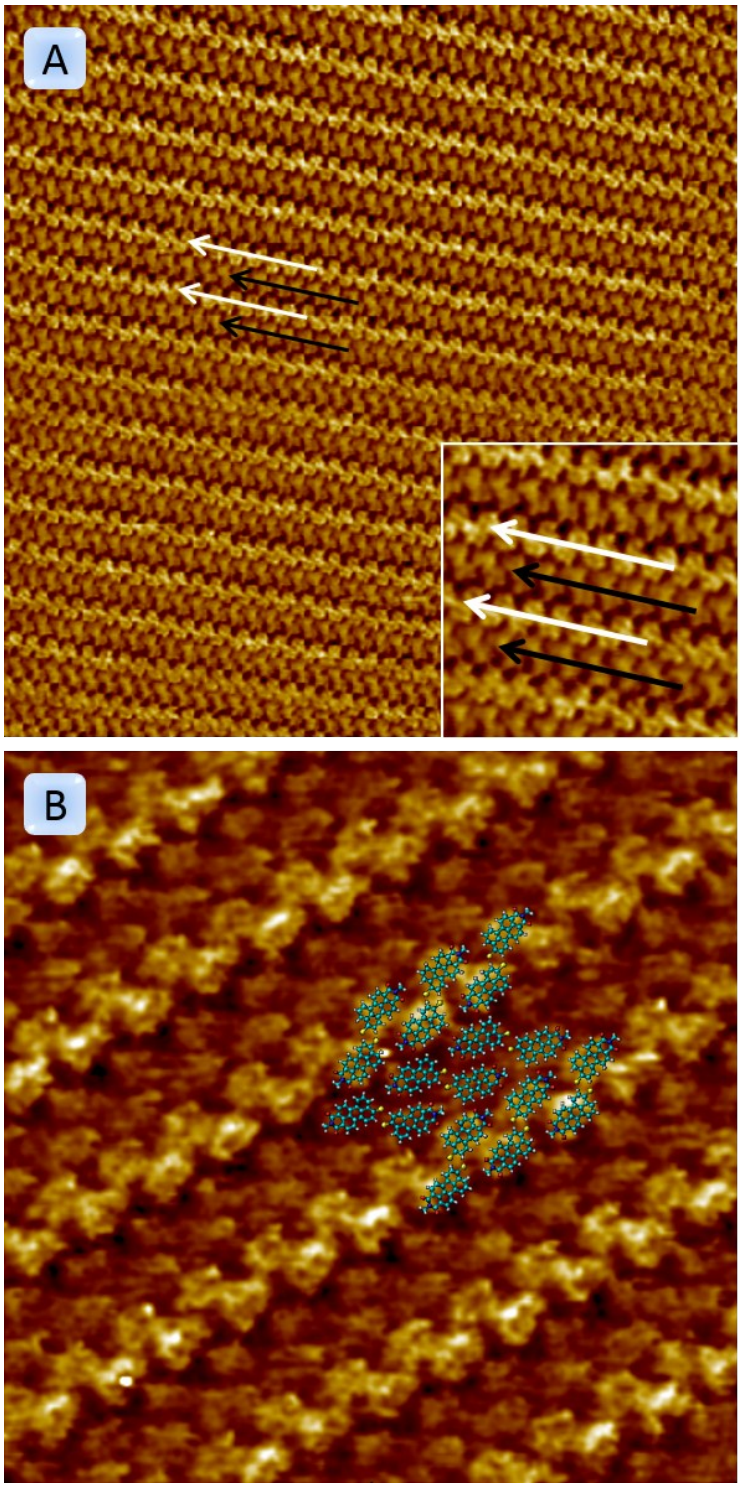


Fig. S8 A) Large scale STM images (60 × 60 nm^2) and B) High resolution STM images (15 × 15 nm^2) of Br-PMI at the 1-phenyloctane-HOPG interface. Imaging conditions: A) I_{set} = 130 pA , V_{bias} = – 550 mV; B) I_{set} = 130 pA, V_{bias} = – 550 mV.

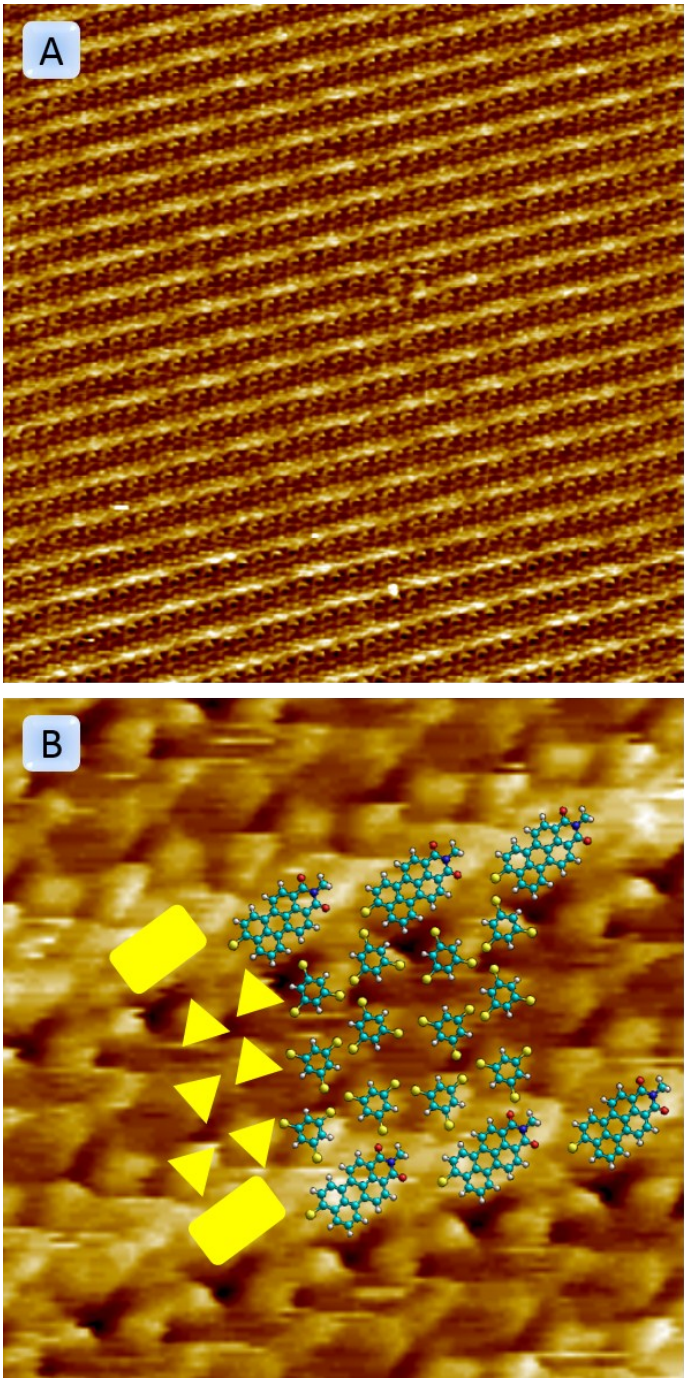


Fig. S9 A) Large scale STM image (60 × 60 nm^2) and B) High resolution STM image (8 × 8 nm^2) of Br-PMI & TBB at the 1-octanoic acid/HOPG interface. Imaging conditions: I_{set} = 80 pA, V_{bias} = – 750 mV.

Reference:

[1] F. Nolde, W. Pisula, S. Müller, C. Kohl and K. Müllen, *Chem. Mater.,* 2006, **18**, 3715.